



(11) **EP 1 260 603 A2**

(12) **European Patent Application**

(43) **Date of Disclosure:** Nov. 27, 2002
Patent Journal 2002/48

(51) **Int Cl.7:** C23C 14/02, C23C 14/06,
C23C 14/35

(21) **Number of Application:** 02011204.1

(22) **Date of Application:** May 21, 2002

(84) **Declared Contract States:**
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR
Declared Extended States:
AL LT LV MK RO SI

(30) **Priority:** DE 10124749

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(54) **Combination procedure for coating, magnetic field supported high capacity pulsed cathodic sputtering and unbalanced magnetron**

(57) A PVD procedure for the coating of a substrate, whereby the substrate has been pretreated by a pulsed, magnetic field reinforced cathodic sputtering process, wherein the said pretreatment at the magnetic field reinforcement made use of a magnetic field arrangement in accord with the magnetron cathode system with a strength of the horizontal components before the target being ca. 100 to 1500 Gauss, following the said pretreatment, an additional coating by means of cathodic sputtering takes place and the power density of the pulsed discharge during the pretreatment lay in excess of 1000 W/cm².

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Description

[0001] The combination of a cathodic arc discharge and an unbalanced magnetron [1,2] for coating of components and construction elements, which are subjected to severe wear, has proved itself as very effective [3] in industrial applications. The high percentage, ionized metal ions, which had been produced within the vapor of the cathodic arc discharge, were employed for the low energy ion implantation with typical acceleration potential on the substrate: 1.2 kV, in order to create ideal conditions to produce a tight layer adhesion. In special cases it has been possible to achieve an even localized, epitaxial layer growth [4]. When this is done, the attack of the substrate surface with Cr-ions had been exceptionally effective [5]. The reasons for this are, that first, excellent adherent characteristics were attained and second, the occurring macroparticulate, namely "droplets" appeared as very small. That is to say, small in comparison to macroparticulate in the case of cathodic arc discharge from materials with low melting points, such as Ti or TiAl [6].

[0002] However, in many areas of applications of tool coating, these macroparticles continue to accumulate during coating with the unbalanced magnetron and become essentially, oversized growth defects. Even though macroparticles operate in a subordinate role, they are given considerable advantage, where corrosion protection [7] is needed or if dry-machining of case-hardened steel shapes (HRC – 60) is concerned. In such applications, the reliability of coating and freedom from porosity are deemed to be important.

[0003] Up to this time, in the field of industrial coating by Physical Vapor Deposition (hereinafter, PVD), process oriented production of greater metal ion thicknesses was a practical operation only with the aid of the cathodic arc discharge. Presently, the magnetic field supported, pulsed cathodic sputtering is gaining in importance. Upon the application of power densities greater than 1000 W/cm^2 , it became possible to generate metal vapors in which up to 60 % of the metal atoms are ionized [8]. This value is comparable with degrees of ionization of metal vapors in the cathodic arc discharge. Fig. 1 shows an optical emission spectrum of a plasma, which was produced in a

[0004] pulsed discharge with Cr as the target, with a power density of 3000 W/cm^2 at a peak voltage of 1200 V, a pulse duration of 50 μs and a pulse interval of 20 ms. The decisive advantage of this kind of metal ion production is to be found therein, in that the procedure eliminates the formation of macroparticulate ("droplets"), and the formation of growth defects as a result of nucleate agglomeration of the said macroparticulates is repressed.

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[0005] In accord with the invention, at the present time the portion of the cathodic arc discharge as an element of the ABS technology is being replaced by a magnetic field supported high-capacity, pulsated, cathodic sputtering source. Correspondingly, the procedures which acted on the substrate in pretreatment remain unchanged. The negative acceleration voltages necessary for the achievement of the etching-effects and ion implantation remain unchanged and typically lie between 0.5 and 1.5 kV. In the case of the preparation of tool steel or metal hardened with Cr-ions, the accelerating voltage remains (negative bias-voltage) unchanged at -1.2 kV [4]. The coating which follows immediately thereafter with an unbalanced magnetron in the non-pulsated operation remains in like manner unchanged, because conventional current supplies assure an efficient yield of energy and lower costs of equipment.

[0006] A series of publications regarding pulsated current supplies for the operation of cathodic sputtering sources is already available. A typical arrangement is described in [9]. This source is, however, exclusively for the coating and has not been developed for the pretreatment of substrates.

[0007] Literature:

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- [2] Wolf-Dieter Münz, C. Schönjahn, H. Paritong, I. J. Smith, LeVide No. 297, Vol. 3/4, 2000, pp 205-223
- [3] W.-D Münz, I. J. Smith, SVC 42nd Ann. Tech. Cont. Proc., Chicago, IL, April 17 to 22, 1999, pp 350-356
- [4] C. Schönjahn, L. A. Donohue, D. B. Lewis, W.-D Münz, R. D. Twesten, I. Petrov, Journal of Vacuum Science / Technology, Vol. 18, Issue 4, 2000, pp. 1718 to 1723
- [5] W.-D Münz, Patent Application: Cr-etching, 1995. Further data (?)
- [6] W.-D Münz, I. J. Smith, D. B. Lewis, S. Creasy, Vacuum, Vol. 48, Issue 5, 1997, pp 47, 481
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- [8] A. P. Ehasarian, K. M. Macak, R. New, W.-D Münz, U. Helmersson, paper to be presented at the 48th International Symposium, IUVSTA 15th International Vacuum Congress, Oct./Nov. 2001, San Francisco, CA
- [9] V. Kouznetsov, PCT Application: WO 98/40532, EP 1038045

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CLAIMS

Claimed is:

1. A PVD procedure for the coating of substrates, whereby the substrate is pretreated in a vapor of a pulsating, magnetic field reinforced, cathodic sputtering, and that during the said pretreatment, for the magnetic field reinforcement, a magnetic field arrangement of the order of a magnetron cathode is employed with a strength of the horizontal component before the target being 100 to 1500 Gauss and that following the said pretreatment, an additional coating by means of cathodic sputtering is carried out, therein characterized in that the power density of the pulsating discharge at the pretreatment lies at a value greater than 1000 W/cm^2 .
2. A procedure, therein characterized, in that the power density preferably lies in the area of 2000 to 3000 W/cm^2 .
3. A procedure, therein characterized,
in that the pulse duration lies between 10 and $1000 \mu\text{s}$ and
in that, the pulse interval runs between 0.2 ms and 1000 s.
4. A procedure, therein characterized, in that duration of the pulse is preferably at $50 \mu\text{s}$ and the pulse interval lies at 20 ms.
5. A procedure, therein characterized, in that the discharge in accord with the magnetron discharge is distributed over the cathode surface, and fills at least 50 % of the said surface.
6. A procedure in accord with claim 5, therein characterized, in that the discharge extends itself over 70 to 90 % of the cathode surface.
7. A procedure, therein characterized, in that average pulsated discharge current density runs less than 10 A/cm^2 .
8. A procedure, therein characterized, in that the local maximum pulsated discharge current density is less than 100 A/cm^2 .
9. A procedure, therein characterized, in that produced pulses carry a peak voltage of 0.5 to 2.5 kV.

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10. A procedure, therein characterized, in that the pretreatment with magnetic supported cathodic sputtering takes place in a non-reactive atmosphere, for example in Ne, Ar, or Xe with the targets of Cr, V, Ti, Zr, Mo, W, Nb, Ta.
11. A procedure, therein characterized, in that the pretreatment with Ar takes place in a pressure range of 10^{-5} to 10^{-1} bar.
12. A procedure, therein characterized, in that a pretreatment with Ar at 10^{-3} takes place.
13. A procedure in accord with claims 1 to 12, therein characterized, in that the substrate, during the pretreatment, receives a negative prevoltage in the range of 0.5 to 1.5 kV of such a type that an etching, that is, a cleaning process and simultaneously an ion implantation process is released (ABS Technology).
14. A procedure in accord with claim 13, therein characterized, in that the negative prevoltage is pulsed with pulse widths of 2 μ s to 20 ms and a pulse interval of likewise, 2 μ s to 20 ms.
15. A procedure, therein characterized, in that the coating with cathodic sputtering is done from the nitrides TiN, ZrN, TiAlN, TiZrN, TiWN, TiNbN, TiBN, or from the carbo-nitrides, TiCN, ZrCN, TiAlCN, TiZrCN, TiVCN, TiNbCN, TiTaCN, TiBCN.
16. A procedure in accord with claim 15, therein characterized, in that the coating contains 0.1 to 5 at% of the fine earths, Sc, Y, La, Ce.
17. A procedure, therein characterized, in that the coatings consist of fine (nano-scale) multiple layers with a periodicity of 1 to 10 nm from the group TiN/TiAlN, TiN/VN, TiN/NbN, TiN/TaN, TiN/ZrN, TiAlN/CrN, TiAlN/ZrN, TiAlN/VN, CrN/NbN, CrN/TaN, CrN, TiN, Cr/C, Ti/C, Zr/C, V/C, Nb/C, Ta/C.
18. A procedure in accord with claim 16, therein characterized, in that one of the engendered single layers contains 0.1 to 5 at% for the rare earths Sc, Y, La, Ce.
19. A procedure in accord with claim 16, therein characterized, in that two of the engendered single layers contains 0.1 to 5 at% of the rare earths Sc, Y, La or Ce.

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20. A procedure, therein characterized, in that the cathodic sputtering employed during the coating is done in the manner of the unbalanced magnetron.
21. A procedure, therein characterized, in that for the pretreatment and the coating, identical cathodes and identical magnetic field arrangements were employed.
22. A procedure in accord with claim 21, therein characterized, in that individual matches of the magnetic field strength for the optimizing of the pretreatment and adjustment of the separating distance of the magnet arrangement from the target surface were carried out.

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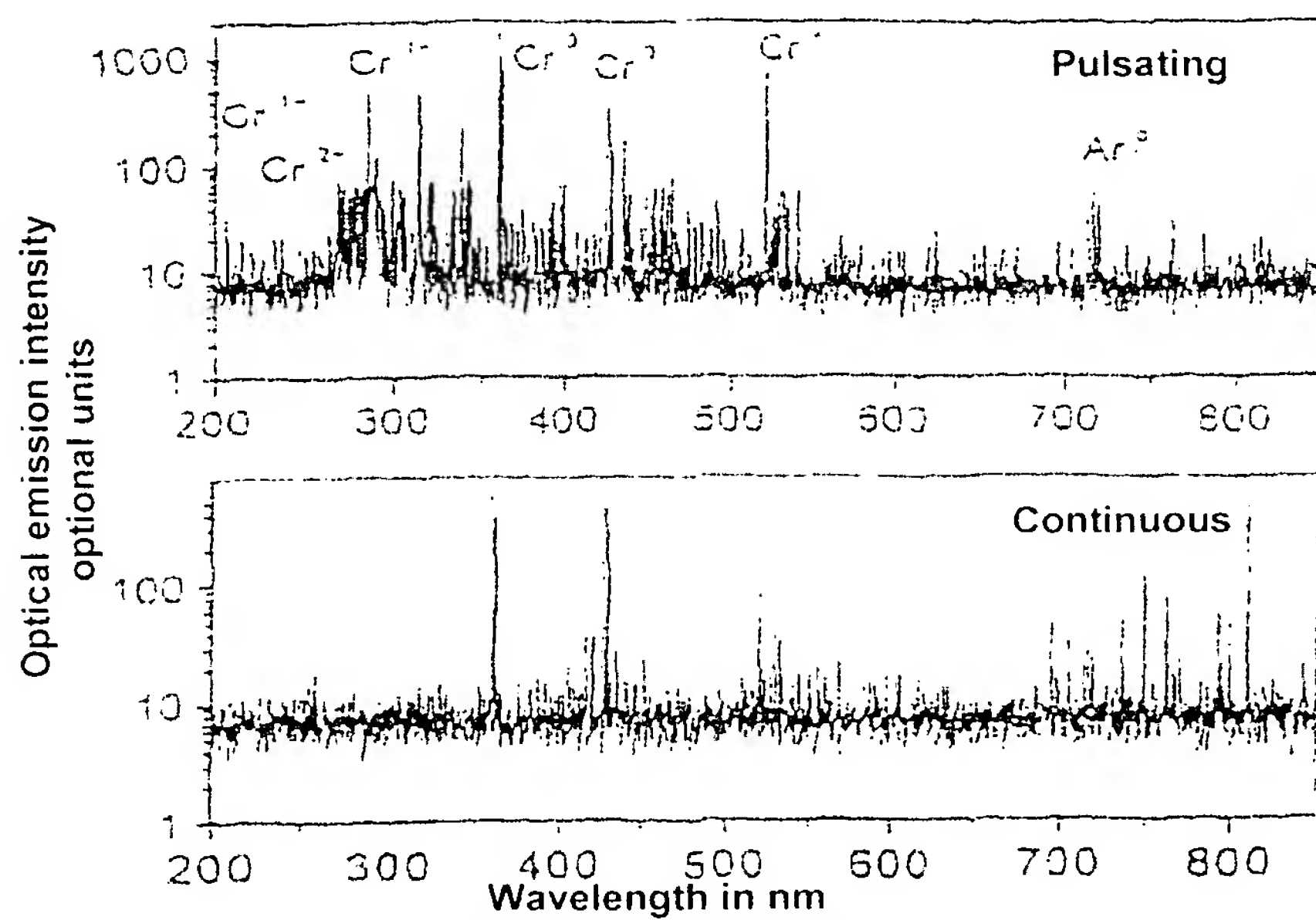


Fig. 1: A comparison between optical emissions produced first, by a high powered, pulsed sputtering and a continuous sputtering of plasma, with an average power input of 100 W.

(19)



European Patent Office



(11)

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(12)

European Patent Application

(88) Day of publication A3
June 2, 2004 Patent Journal: 2004/23

(43) Day of publication A2
Nov. 27, 2002 Patent Journal 2002/48

(21) Application Number: 02011204.1

(22) Day of Application: May 21, 2002

(51) Int Cl.7: **C23C C23C 14/00, C23C 14/35
C23C 14/02**

(84) **Declared Contract States:**
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE TR
Declared Extended States:
AL LT LV MK RO SI

(30) Priority: May 21, 2001 DE 10124749

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European Research Report

No. of Application

EP 02 01 1204

RELEVANT DOCUMENTS			
Category	Designation of the documents with statements, where required, of the defining parts	Involved Claims	Classification of the Application (Int. Cl. 7)
Y, D	WO 98 40532 A (KOUZNETSOV VLADIMIR; CHEMFILT R & D AKTIEBOLAG (SE)) September 17, 1998 * Page 6, Lines 27-30; Claims 1-6 *	1-5 9-11, 13, 15, 20	C23C14/00 C23C14/35 C23C14/02
Y, D	US 6 033 734 A (MÜNZ WOLF-DIETER ET AL) March 7, 2000 * Column 2, Line 65; Claims 1, 5, 6, 11, 17; Table 2 *	1-5 9-11, 13, 15,20	
A	DE 42 06 110 A (HAUZER HOLDING) September 2, 1993		Field of Research
			C23C
The present research report is executed for all patent claims			
<u>Place of research:</u> The Hague		<u>Closing date of the research</u> April 7, 2004	<u>Examiner</u> Laveant, P
<u>Categories of the named documents</u> X : Of particular bearing when considered alone Y : Of particular bearing when consider in combination with another publication of the same category A : Technological background O : Non-written communication P : Interposed literature T : Basic theories of the invention		E : An older patent document, which only on or after the application date has been published. D : A document supplied with the application L : A document furnished on other grounds & : Member of the same patent family, agreeing document	

(Addendum follows)

**Addendum to the European Research Report
In Regard to the European Patent Application EP 02 01 1204**

In this addendum are presented the members of the patent families of the above European Research Report

The statements in regard to the family members represent the opinion of the data of the European Patent Office on April 7, 2004.

These statements serve only for information and carry no responsibility for the European Patent Office.

Patent Document Referred to in the Research Report	Date of Declaration (Publishing of Application)	Member or Members of the Patent Family		Date of the Release
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